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Academia Sinica, Taiwan, 13–16 March 2008

National Tsing-Hua University, Taiwan, 23–25 March 2008

Chinese Academy of Sciences, China, 16 May 2008

Fudan University, China, 21 May 2008

Peking University, China, 21 May 2008

University of Oxford, UK, 28 May 2008

Scope of Research

Crystallographic and electronic structures of materials and their transformations are studied through direct imaging of atoms or molecules by high-resolution spectromicroscopy which realizes energy-filtered imaging and electron energy-loss spectroscopy as well as high resolution imaging. It aims to explore new methods for imaging and also obtaining chemical information in thin films, nano-clusters, interfaces, and even in solutions. By combining this with scanning probe microscopy, the following subjects are urging: direct structure analysis, electron crystallographic analysis, epitaxial growth of molecules, structure formation in solutions, and fabrication of low-dimensional functional assemblies.

Research Activities (Year 2008)

Publications

Kurata H, Isoda S, Tomita K (JEOL): Development of Nanotip Field Emission Gun, *Kenbikyoku*, **42**, 211-213 (2007) (in Japanese).

Haruta M, Yoshida K, Kurata H, Isoda S: Atomic Resolution ADF-STEM Imaging of Organic Molecular Crystal of Halogenated-Cu-phthalocyanine, *Ultramicroscopy*, **108**, 545-551 (2008).

Yoshida K, Jiu J (Osaka Univ.), Nagamatsu D, Nemoto T, Kurata H, Adachi M (Doshisha Univ.), Isoda S: Structure

of TiO₂ Nanorods Formed with Double Surfactants, *Mol. Cryst. Liq. Cryst.*, **491**, 14-20 (2008).

Grants

Kurata H, Development of an EELS/XES Electron Microscope for Electronic Structure Analysis, Leading Project, The Ministry of Education, Science, Culture and Sports, Japan, 1 April 2004–31 March 2007.

Kurata H, Local State Analysis of Defects and Interface Regions by Spherical Aberration Corrected STEM and

Local State Analysis by STEM-EELS Equipped with a Nanotip-FEG

Electron energy-loss spectroscopy (EELS) combined with an aberration corrected scanning transmission electron microscope (STEM) enable to perform local analysis with an atomic resolution owing to a sub-angstrom electron probe with a high probe current. In order to enhance a performance of STEM-EELS analysis, we developed a 200 kV Cs-corrected STEM/TEM equipped with a nanotip-FEG, which produces an incident electron probe of 0.1 nm or less in diameter with an illumination semi-angle of 23 mrad. As an application to STEM-EELS analysis, we carried out local state analysis using the spatially resolved EELS measured from a BaTiO₃ (BTO) thin film grown on SrTiO₃ (STO) substrate. In the vicinity of the interface, a strained structure and a misfit dislocation are observed in the BTO region. The imaginary part of dielectric function (ϵ_2 spectrum) deduced from valence electron excitation spectrum shows the change of electronic structure due to the strain structure near the interface, which is confirmed by a first principles band structure calculation. From the energy-loss near-edge structure of Ti L_{2,3}-edge, the crystal-field strength measured from the separation between t_{2g} and e_g peaks is also slightly different, which indicates that

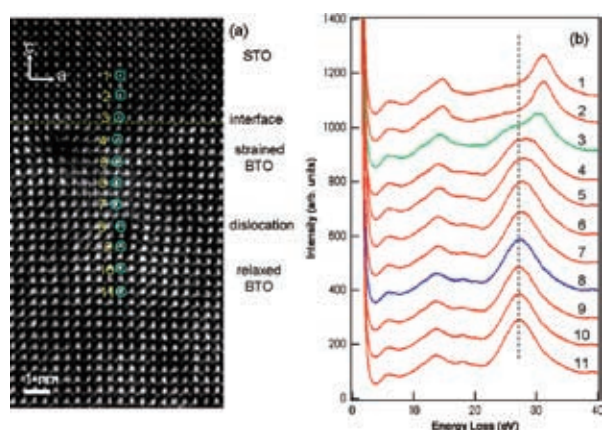


Figure 1. STEM image and spatially resolved EELS measured from the vicinity of the interface of BTO/STO.

the local electronic structure should be changed at the strained and defect regions.

Atomic Resolution ADF-STEM Imaging of Organic Molecular Crystal of Halogenated-Cu-phthalocyanine

Annular dark-field (ADF) scanning transmission electron microscopy (STEM) is a powerful technique for acquiring high-resolution images of materials. High-angle ADF (HAADF) STEM images are considered to be incoherent, showing chemical image contrast (Z-contrast), due to the dominated effect of thermal diffuse scattering (TDS) in the detected signal. However, to date, HAADF STEM imaging has been performed invariably for inorganic crystals. In this report, an ADF-STEM measurement is demonstrated for the first time to be applicable for acquiring Z-contrast images of organic molecules at atomic resolution. The structural image of a molecular crystal of hexadecachloro-Cu-phthalocyanine (Cl₁₆-CuPc) is acquired at atomic resolution by ADF-STEM (Figure 2). In molecular crystals with comparatively large lattice constants, such as the Cl₁₆-CuPc sample examined in this study, low-angle ADF (LAADF) STEM observation with a detection angle of 24–64 mrad was found to be advantageous for acquiring incoherent Z-contrast images similar to the case of conventional HAADF-STEM.

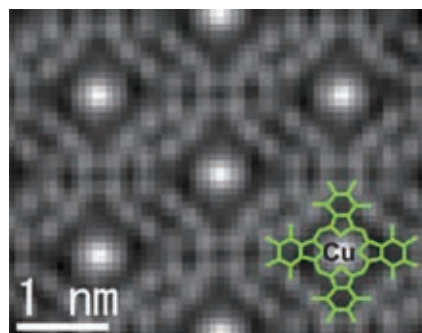


Figure 2. Noise filtered LAADF-STEM image of Cl₁₆-CuPc projected along the c-axis.

EELS, Grant-in-Aid for Scientific Research (B)19310071, 1 April 2007–31 March 2010.

Isoda S, Nanotechnology Support Project, The Ministry of Education, Science, Culture and Sports, Japan, 1 April 2007–31 March 2011.

Isoda S, Development of Observation Method of Polymer Composite Materials without Staining by Scanning Transmission Electron Microscope, Grant-in-Aid for Scien-

tific Research (C) 20550188, 1 April 2008–31 March 2011.

Award

Koshino M, Kurata H, Isoda S, Microscopy and Microanalysis, 2007 Best Materials Paper Award, “Stability Due to Peripheral Halogenation in Phthalocyanine Complexes”, Microscopy Society of America, 10 September 2008.